have resolutions of better than 0.05 *nm* which is about 4000 times better than optical microscopes.

Scanning probe microscopes (SPM) are able to image, characterize and even manipulate material structures at exceedingly small scales including features of atomic proportions. SPM's use no lenses, but rather a very sharp probe (a very small, very sharp needle) that interacts with the sample surface. It maps various interactions and forces which occur between the probe and the surface of the sample to create an image of the sample. These instruments are capable of the resolution which is needed to create atomic level images.

The study of the principle, working and applications of optical microscope, scanning electron microscope (SEM), transmission electron microscope (TEM), scanning tunneling microscope (STM) and atomic force microscope (AFM) is the subject matter of the present chapter. These microscopes are very useful tools for imaging surface of materials and their interior, characterize materials and even manipulate atoms and molecules to be used in building nanoscale devices.

9.2 OPTICAL MICROSCOPY

Optical microscopy is defined as the formation of a magnified image of a small object using visible light (λ = 400 nm to 780 nm) as illumination. It is simple and low cost technique and hence most widely used form of observational instruments. Hans Jansen is said to invent the first compound microscope in Italy at the end of sixteenth century. However, Dutch microscopist Antoni Leeuwenhock is regarded as the father of optical microscopy.

A compound microscope consists of two lenses - an objective lens and the eyepiece lens. The lens towards the object is called the objective lens whereas the lens near our eye while observing a sample or an object is called the eye lens. A microscope works on the principle that the objective lens forms a magnified image of the given object. This image acts as an object for the eyepiece lens which forms a further magnified image of the original object. The final magnification $M\left(=\frac{\text{image size}}{\text{object size}}\right)$ of the microscope is the product of individual magnifications of objective lens (M_1) and the eyepiece lens (M_2) *i.e.*,

$$M = M_1 \, M_2$$

In modern instruments, a group of lenses are used both for objective and for eyepiece lens because single lenses suffer from many defects. The chief characteristic of an optical microscope is its limit of resolution. *It is defined as the minimum distance between two points on a sample (or an object) which can be clearly resolved (distinguished) by the microscope.*

$$\text{Limit of resolution, } \theta = \frac{0.61\lambda}{\text{N.A.}}$$

where N.A. means numerical aperture of the objective lens and is defined as

$$N.A. = \text{Sin}\,\alpha/n$$

where α is half of the acceptance angle of the lens and n is the refractive index of the medium filled between the lens and its focal plane. Thus wavelength of light used for illumination and the numerical aperture of the objective lens determines the limit of resolution of an optical microscope.

The principal **disadvantage of an optical microscope** is its natural resolution limit of 200nm imposed by wavelength of visible light. This theoretical resolution limit was actually achieved by optical instruments around 1880s.

To overcome this limitation, illumination of shorter wavelengths such as UV or *X*-rays may be used. *X*-ray microscopes have been an active area of research but focusing of *X*-rays presents a big problem.

Another solution for the problem of improving resolution better than optical microscopes is provided by the use of material particles e.g. electrons, neutrons, protons etc as the source of illumination due to their wave nature. Electrons, however, are the most favoured form of illumination because they

- Can be produced in a collimated beam easily
- Can be accelerated & focused by electric and magnetic fields
- Highly accelerated (several keV) electrons have very small wavelengths (10^{-12} m) associated with them which produces a resolution sufficient to observe samples on an atomic scale.

The development of optical microscopy owes to a great deal to the German physicist Ernst Abbe, who formalized the theory of image formation in 1877. In 1930s, Zernike developed an advanced form of optical microscopy known as **"phase contrast microscopy"** which allows details to be seen in thin transparent sections which are not visible using standard microscopy and confocal microscopy. **Confocal scanning optical microscopy** is an advanced optical microscopy which produces 3D images.

Optical microscopy has several applications such as

- Observation of biological samples
- Metallographic observations
- Quality control in electronics industry etc.

Let us now understand the basic principles of optical microscopy:

9.2.1 Compound Microscope

As stated above, a compound microscope is a combination of two lenses- an objective lens and a eyepiece lens. In fact, in modern microscopes objective lens system comprises of a group of several lenses and so is the case with eyepiece lens system. This is done to minimize aberrations and distortions. The real and magnified image of the object formed by the objective serves as the object for the eyepiece lens which forms a further magnified virtual image of the object as shown in fig. 9.1.

maxima and minima. According to Abbe, no combination of waves of a given wavelength λ can result into concentrating all the intensity into a zone $\leq \lambda/2$. This size is achieved if plane waves of equal amplitude arrive at a point from all directions.

A plane wave arriving at a lens, will be focused into a disc at least $\lambda/2$ in diameter, no matter how good the lens is. This disc is called the Airy's disc. The size of the disc will be larger than $\lambda/2$ if

(i) Lens diameter < lens focal length, and

(ii) A small aperture is centered on the principal axis near the lens.

The above discussion clearly shows that it is not possible to concentrate all the light in a single spot.

9.2.3. Rayleigh's Criterion of Resolution

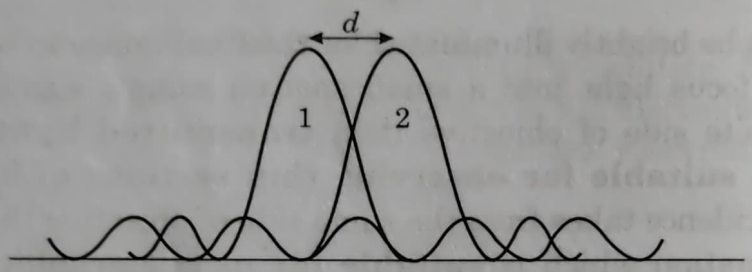


Fig. 9.3. Rayleigh's Criterion

- Rayleigh's criterion of resolution says that two nearby points are just resolved, if the distance between the intensity maxima in their images is at least equal to the distance from the central maximum to the first minimum in one of the images. This distance ($\approx M\lambda/2$) gives the limit of resolution of the microscope (fig. 9.3).
- The resolving power (1/limit of resolution) of the lens approaches this theoretical optimum as its D/f ratio increases.
- Modern objective lenses have very small f with large α which gives $\sin\alpha$ around 0.9. Thus for air ($n = 1$), N.A. $= \sin\alpha = 0.9$ (maximum).
- Oil immersion objectives (n=1.5), have N.A. upto 1.4 which gives limit of resolution to 200nm.

9.2.4. Defects in Lenses

Lenses suffer from various defects and aberrations, distortions etc. Spherical aberration means focusing of paraxial and marginal rays at different points on the principal axis of the lens. Due to chromatic aberration light of different colours is focused in different planes. As a result we get coloured image for a white object. Due to field curvature of the lens, different parts of the object are focused in different image planes. Image distortion results in the straight lined portions of the object to appear skewed in the image.

These defects can be removed by careful design of lenses. But these objective lenses become very expensive.

9.2.5. Sample Preparation

(i) For metallurgical studies, high quality polishing or chemical etching is required.

(ii) For biological tissues few microns thick slices are cut by microtome and either stained or marked with fluorescent compounds to produce higher contrast.

It should be noted that careful sample preparation results in better quality and makes interpretations easy.

9.2.6. Image Contrast

Variations in the local intensity of light in the image plane is called the contrast. In optical microscopy, contrast occurs due to absorption and scattering of light by the sample. Parts of the sample that absorb strongly appear dark in the image and those scatter strongly appear bright. When the incident illumination is axial, it forms "bright field" image and when it is off axis, "dark field" image is formed.

An object appears bright or dark depending upon how it was prepared and how it is illuminated.

An advanced version of optical microscopy known as **phase contrast microscopy** is based on the interpretation of contrast. It is the technique for increasing the contrast from unstained thin biological specimens without sacrificing resolution.

Conclusively we can say that, resolving power of an optical microscope primarily depends upon its numerical aperture and wavelength of illumination. Secondary factors that affect resolution are :

1. Type of specimen
2. Coherence of illumination
3. Degree of aberration correction
4. Contrast enhancing methodology.

9.3 FLUORESCENCE MICROSCOPY

The absorption and subsequent re-radiation of light by organic and inorganic substances is called **fluorescence** or **phosphorescence**. In fluorescence, the emission of photon (light) is nearly simultaneous with its absorption with a time delay of less than 1μs between the two processes. However in phosphorescence, the light emission persists longer after the illuminating light (excitation) has been extinguished. Fluorescence was first observed by Sir Geroge Gabreil Stokes in 1852. Its physical explanation was given by Alexander Jablonski in 1935. Fluorescence is the only mode in optical microscopy in which the specimen subsequent to excitation produces its own light. Minerals, crystals, resins, butter, chlorophyll, vitamins, and inorganic compounds fluoresce upon excitation with ultraviolet (UV) light. Fluorescence emission occurs at a longer wavelength than that of the excitation light. This is called **Stokes' shift**. As Stokes' shift value increases, it becomes easier to separate excitation from emission light through the use of fluorescence filter combination.

Fluorescence microscopy is a special case of optical microscopy that uses fluorescence and phosphorescence instead of or in addition to absorption and reflection to investigate the properties of organic or inorganic substances. It is an essential tool in biology and bio-medical sciences, and materials science. In life sciences, fluorescence microscopy is a powerful tool for specific and sensitive staining of a specimen to detect the distribution of proteins or other molecules.

Principle of Fluorescence Microscopy

In fluorescence microscopy the specimen is stained with chemical substances capable of emitting their own light after being excited with light of suitable wavelength. These substances are called **fluorochromes** and possess adequate absorption properties and emission quantum yields. The principle of fluorescence may be understood as follows:

1. Atoms of the specimen absorb energy (from excitation) to become excited
2. Electron in the atom jumps to higher energy level
3. Soon the electron relaxes to the lower level (ground state) by emitting photon *i.e.*, light. The result is that the atom is fluorescing.

In fluorescence microscopy light of specific wavelength(s) is used for the excitation of the specimen. Due to fluorescence, emission of light of longer wavelength from the specimen occurs. Spectral emission filters are employed that separate out illumination light (excitation) from the much weaker fluorescence light. Emitted light make up the image of the specimen surface.

Components of a Fluorescence Microscope

A fluorescence microscope is so powerful that it can even reveal the presence of a single molecule. It consists of

(i) Light source such as xenon arc lamp, and mercury vapour lamp. Advanced microscopes use high power LEDs and lasers.

(ii) Excitation filter that selects the light of the particular colour (given out by the polychromatic source) which is to be used for exciting the specimen.

(iii) Dichroic mirror (or dichromatic beam splitter)

(iv) Barrier (or Emission) filters that separate out weaker emitted light from the much brighter excitation light.

Cameras used in fluorescence microscopy should offer :

(i) High signal intensity

(ii) Low noise, and

(iii) Ability to quantify intensity of intensity distribution.

Light Sources

In fluorescence microscopy the light source utilized for excitation be of sufficient brightness so that the weak emission light can be maximized. It requires intense,

Quenching is an excited state relaxation process which results in reduced fluorescence intensity. Quenching occurs as a result of oxidizing agents or the presence of salts or heavy metals or halogen compounds. It involves non-radiative energy loss for example conversion to heat. It also results due to transfer of energy to another molecule i.e. from donor to acceptor. The process is termed as fluorescence resonance energy transfer (FRET).

Fluorescence resonance energy transfer and fluorescence recovery after photobleaching are very powerful tool for the study of individual fluorophores and fluorescently labeled molecules.

Advantages of Fluorescence Microscopy

- Fluorescence microscopy is the most popular cell and molecular biological research tool to study dynamical changes occurring in the cell
- It is a highly sensitive technique and can detect a few molecules per cubic micrometer
- Fluorescence microscopy provides high contrast imaging and high resolution
- It provides possibility to use different colours to track distinct molecules
- Quantitative imaging is possible.

Drawbacks/ Limitations

- Due to photobleaching, fluorophore lose their ability to fluoresce as they are illuminated. Chemical destruction of fluorophore taking place during excitation is called photobleaching. Photobleaching can severely limit the time of observation of a sample by fluorescent microscopy. Photobleaching can be lowered by using robust fluorophore, by minimizing illumination, or by using photo protective scavenger chemicals
- Cells are prone to photo toxicity especially when a short wavelength is used for excitation. Fluorescent molecules tend to generate reactive chemical species when being illuminated, increasing the phototoxic effect
- In biological samples autofluorescence is a large problem which cannot be removed by excitation/ emission filters
- Fluorescence microscopy only allows observation of the specific structures which have been labeled for fluorescence
- Fluorescence microscopy cannot be used for examining non-living cells.

Applications

- Fluorescence microscopy can be used for identification of different cells and other cellular components which are not possible through the simple optical microscopy
- For simultaneous identification of various different molecules in the targeted specimen or the sample

Metal tip for field ion microscope is prepared by electrochemical polishing of thin wires. The final preparation procedure involves the in-situ removal of asperites by field evaporation by increasing tip voltage.

Applications

Field ion microscopy can be applied to only those materials which (i) can be fabricated in the form of a sharp needle, (ii) can withstand high electrostatic fields, and (iii) can be used in ultra high vacuum environment. Because of these limitations refractory metals (W, Mo, Pt, Ir) that have high melting points are suitable materials for making tip of the field ion microscope.

Field ion microscopy is used to study the dynamical behavior of surfaces and the behavior of adatoms on surfaces. It can be used to image the arrangement of atoms at the surface of a sharp metal tip. Field ion microscope has been used for the study of

(i) adsorption-desorption phenomena

(ii) surface diffusion of adatoms and clusters

(iii) adatom-adatom interactions

(iv) equilibrium crystal shape, and

(v) step motion etc.

Field ion microscopy can reveal atomic structure of dislocation or grain boundaries. It also allows the observation of second phase particles and provides information about size, shape, volume fraction etc. It is utilized to observe metals and some semiconductors when atomic resolution is desired.

Limitations

- FIM provides only black & white micrographs and no chemical information is obtained
- Inability to identify chemical nature of the individually imaged atoms.

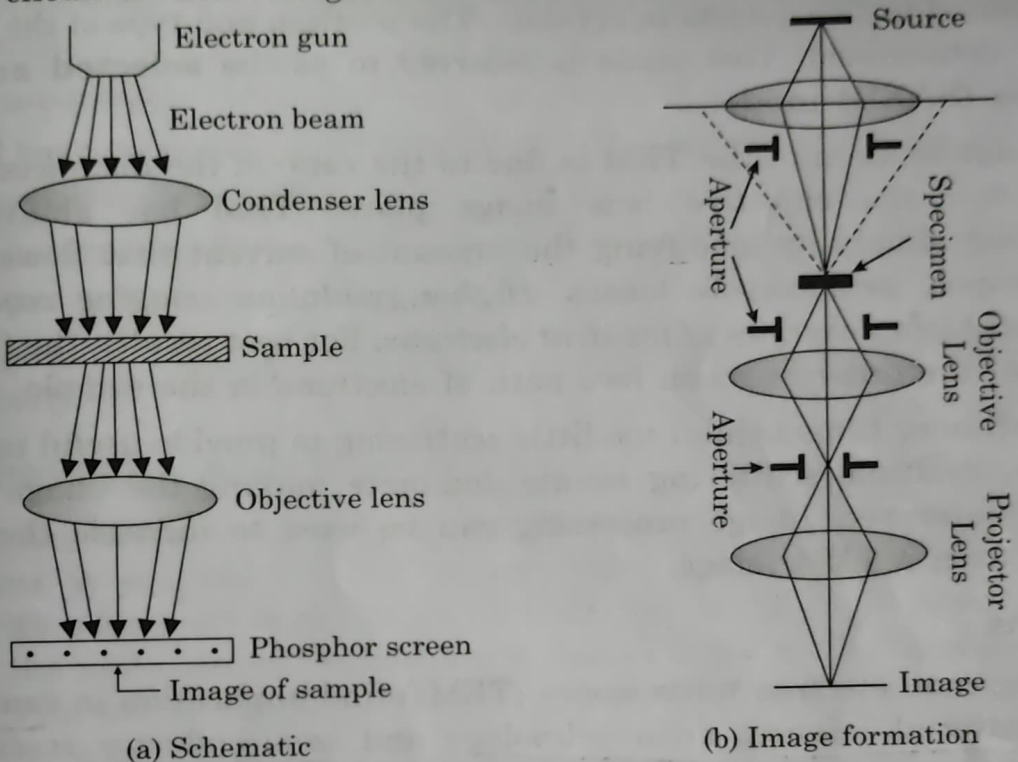
9.5. TRANSMISSION ELECTRON MICROSCOPE

Electrons can be produced, focussed, accelerated to high energies and converted into a collimated beam easily. These highly energetic electrons have wavelengths of the order of picometers (10^{-12} m). A transmission electron microscope (TEM) uses energetic beam of electrons to provide topographical, morphological, compositional and crystallographic information on samples or specimens. The first TEM was built by Max Knoll and Ernst Ruska in 1931.

In the TEM experiments a focussed beam of electrons is transmitted through an ultra-thin specimen under ultra-high vacuum ($\approx 10^{-4}$ Pa), interacting with the atoms of the specimen as it passes through it. An image is formed from the

interaction of the electrons transmitted through the specimen. This image is magnified and focussed onto an imaging device, such as a fluorescent screen, on a layer of photographic film or it is detected by a sensor like a charge coupled device (CCD). **TEM has a higher resolution ($\approx 0.05\ nm$) due to small de Broglie wavelength of electrons**. This enables TEM to capture fine details even as small as a single column of atoms.

TEMs produce high resolution, two-dimensional images which gives it a wide range of educational, science and industry applications. It is a major analytical tool in physical, chemical and biological sciences.



(a) Schematic (b) Image formation

Fig. 9.6. Transmission Electron Microscope

Principle : A transmission electron microscope (TEM) consists of an emission source (tungsten filament or LaB_6 source). Materials with either a high melting point such as tungsten, or those with a low work function (LaB_6) are required for the gun filament. The electron gun is given a high voltage (100 – 300kV) and it emits electrons by thermionic emission or by field electron emission. The electrons are focussed by an objective lens, are amplified by a magnifying (projector) lens, and finally produce the desired image on a screen. The basic principle of a conventional TEM is shown in Fig. 9.6 (a) and its ray diagram is shown in Fig. 9.6 (b).

The electromagnets manipulate the electron beam. Electrostatic fields also deflect the electron beam through a constant angle. These two opposing deflections give rise to a shift in the path of the beam. Images are formed because different atoms interact with and absorb electrons to a different extent. The observed image depends upon the **amplitude of electron beam** as well as on the **phase of electrons.**

The most common mode of operation for a TEM is the **bright field imaging mode**. The contrast is formed directly by occlusion and absorption of electrons in the sample. Thicker regions of the sample, or regions with a higher atomic number will absorb more and hence appear dark, while regions with no sample in the beam path will appear bright. Hence the name bright field imaging given to this mode. The image is formed due to undeviated transmitted electron beam.

Another mode of operation of TEM *i.e.*, **diffraction image observation mode** is the one in which the contrast is produced by the Bragg scattering (diffraction) of electrons by the atoms of the crystalline sample. This method can be used for identification of lattice defects in crystals. The position and type of the defect can be accurately determined. This mode is referred to as the **selected area electron diffraction (SAED) mode**.

The magnification of the TEM is due to the ratio of the distances between the specimen and the objective lens image plane. TEM has ability to change magnification simply by modifying the amount of current that flows through the coil, quadrupole or hexapole lenses. *Higher resolution imaging requires thinner samples and higher energies of incident electrons*. For best results, the film thickness should be of the order of mean free path of electrons in the sample.

Much thinner films exhibit too little scattering to provide useful images, and in thick films, multiple scattering events dominate making the image blurred and difficult to interpret. Image processing can be used to increase the information obtainable from a TEM image.

Applications

Transmission electron microscopes (TEMs) find application in cancer research, virology, material science, nano-technology and semiconductor research. Lattice structure of the material can be determined by TEM. The shape of the sample can be determined from the image. TEMs can be used to detect flaws, fractures and damages to micro-sized objects. Imaging capabilities of TEM are aided (complemented) by diffraction patterns for structural studies and spectroscopic techniques for chemical analysis.

Advantages

1. Transmission electron microscopes (TEMs) provide most powerful magnification of one million times or more.
2. It has wide range of applications in educational, scientific and industrial fields.
3. TEM can provide information on element and compound structure.
4. It forms detailed and high quality image of samples. It produces highest resolution images.

5. Easy operation.
6. Yield information of surface features, shape, size and structure.

Drawbacks

1. TEMs are large and very expensive.
2. Extensive sample preparation is required to produce a sample thin enough (10 to 100 nm) to be electron transparent. Producing thin samples is quite difficult and these may not represent the larger object to which they belong.
3. TEM analysis is a relatively time consuming process and requires special training.
4. The sample may be damaged by the electron beam.
5. TEM has a relatively small field of view. Thus at a time a very small portion of the specimen is observed.
6. The structure of the sample may get changed during the sample preparation process.
7. Complicated contrast mechanisms which makes image interpretation difficult.

9.6. SCANNING ELECTRON MICROSCOPE

The scanning electron microscope (SEM) is a tool for the characterization of nano-structures. A scanning electron microscope produces images of a sample by scanning it with a focussed beam of electrons. The image consists of the variation as a function of the probe position, of some signal generated by the sample under the probe. The interaction of the electrons with the atoms of the sample produce various signals which contain information about the surface topography of the sample and also about the composition of the sample. Various signals produced by a scanning electron microscope are :

1. Secondary electrons (SE)
2. Reflected or back scattered electrons (BSE)
3. Photons of characteristic X-rays or light
4. Absorbed current (*i.e.*, specimen current) and transmitted electrons.

The specimen in SEM should be completely dry. The samples in an SEM can be solid or bulk specimens of any size that will fit within the specimen chamber. Specimens can be studied in low vacuum, high vacuum, wet conditions and at a wide range of very low or elevated temperatures. Both **conductive and non-conductive samples** can be studied with the help of a SEM. A scanning electron microscope can achieve a resolution better than 1 *nm*. A very narrow electron beam used in SEM results in a large depth of field of scanning electron microscope micrographs (images).

Construction

The basic principle of a SEM is shown in Fig. 9.7(a) and its schematic diagram is shown in Fig. 9.7(b). It consists of an electron gun fitted with a tungsten filament cathode from which electrons are thermionically emitted. Tungsten is suitable for making cathodes because of its high melting point and low vapour pressure. The low cost also goes in favour of tungsten.

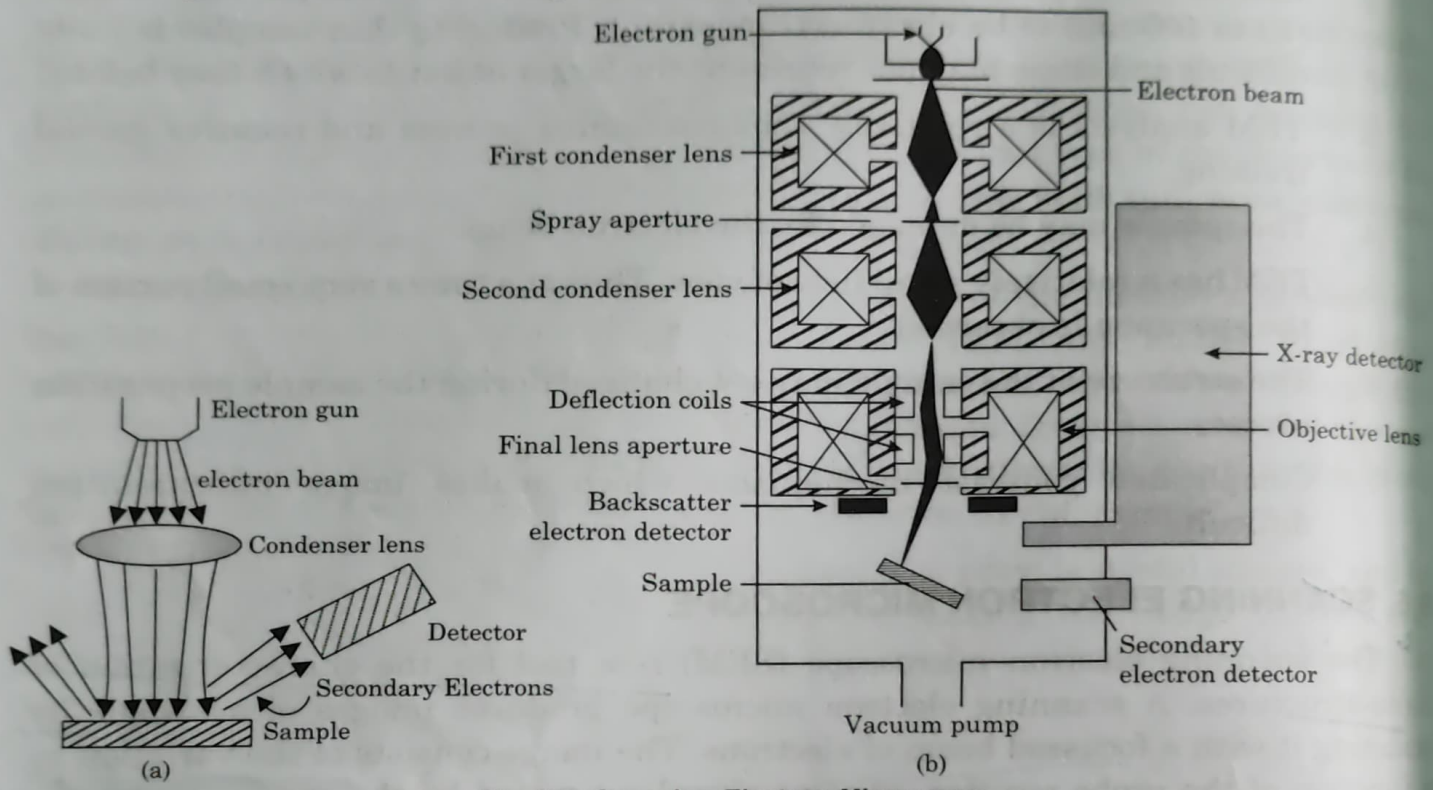


Fig. 9.7. Scanning Electron Microscope

A set of condenser lenses is used to focuss the electron beam into a narrow spot. Pairs of scanning coils or deflector plates are used to deflect the electrons into x or y direction so that the electron beam scans the sample in a raster fashion over a rectangular area of sample surface. **Rectangular pattern of image capture and reconstruction is called raster scanning**. A number of detectors such as secondary electron detector, X-ray detector, backscatter electron detector etc. are also a part of the scanning electron microscope. These detectors are used to receive various signals emitted from a scanning electron microscope when an energetic beam of electrons falls over the specimen.

Working

A scanning electron microscope combines the ease of operation of an optical microscope and the analysis capacities of a TEM. In a typical scanning electron microscope, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. This cathode is electrically heated for the emission of electrons. The low energy (0.2 keV to 40 keV) electron beam is focussed by one or two condenser lenses to a spot of 0.4 nm to 5 nm in diameter. This focussed

beam of electrons is then passed through a system of magnetic lenses used for the deflection of beam in the x and y directions. Thus a rectangular area of the surface of the sample is scanned by the electron beam. The resulting image is a distribution map of the intensity of the signal being emitted from scanned area.

The energy exchange between electron beam and the specimen gives rise to the reflection of high energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation (*i.e.*, X-rays). The various interactions between electron beam and sample and the signals produced therein are shown in Fig. 9.8. Now we discuss various detection modes of an scanning electron microscope one-by-one.

1. Secondary Electron Imaging (SEI) : This is the standard detection mode of an scanning electron microscope. This mode collects **low energy (< 50 eV) secondary electrons** that are ejected from the K-shell of the specimen atoms by **inelastic scattering** interactions with beam electrons. These electrons originate within a few nanometer from the sample surface. This is why SEM operation in the SEI mode can produce very high resolution images of a sample surface. Secondary electrons are detected by an Everhart-Thornley detector, which is a type of scintillator photo-multiplier system. Steep surfaces and edges tend to be brighter than flat surfaces, which results in images with a well defined, three-dimensional appearance. Using the secondary electrons, **image resolution of less than 0.5 *nm* is possible.** The brightness of the signal depends on the number of secondary electrons reaching the detector.

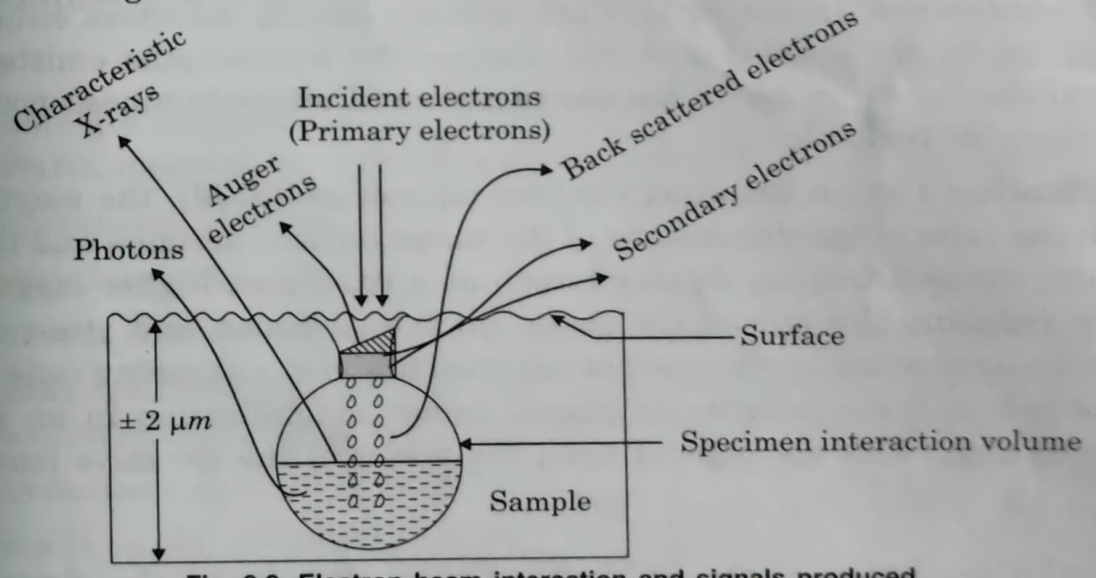


Fig. 9.8. Electron beam interaction and signals produced

2. Back Scattered Electron (BSE) Imaging : Back scattered electrons (BSE) are **high energy electrons** that originate in the electron beam and are reflected or back scattered out of the specimen interaction volume by **elastic scattering** interactions with atoms of the specimen. Back scattered electrons emerge from **deeper locations** within the specimen and consequently the BSE resolution is

poorer than secondary electron images. Heavy elements (*i.e.*, high value of atomic number Z) back scatter electrons more strongly than light elements, therefore BSE **are used to detect contrast between areas with different chemical compositions**. Back scattered electron detectors are either of scintillator or of semiconductor type. Strong topographic (*i.e.*, surface) contrast is produced by collecting back scattered electrons from one side of the specimen using an asymmetrical directional BSE detector. Back scattered electrons are used in analytical SEM along with the characteristic X-ray spectra as BSE signal intensity is strongly related to atomic number Z of the specimen. BSE images can **provide information about the chemical composition of the sample**. Back scattered electrons can also be used to determine the crystallographic structure of the specimen. Thick specimens can be studied by detecting back scattered electrons.

3. Characteristic X-ray : Characteristic X-rays are emitted when the electron beam removes an inner shell (K, L, M,...) electron from the sample and a higher energy electron from any of the outer shell jumps into the vacancy and difference of energy is released as X-rays. These X-rays are useful in determining the composition and abundance of elements in the sample.

4. Cathodoluminescence : The emission of light when atoms excited by high energy electrons return to their ground state, is called Cathodoluminescence. High energy electrons in the electron beam in an SEM can cause valence band electrons to jump into conduction band in a semiconductor material leaving behind holes. In a direct band gap material, recombination of the electron-hole pairs (EHPs) will result in cathodoluminescence. In the SEM, Cathodoluminescence detectors either collect all light emitted by the specimen or can analyse the wavelengths emitted by the specimen and display an image of the distribution of Cathodoluminescence emitted by the specimen in real colour.

Magnification : In an scanning electron microscope (SEM), the magnification results from the ratio of the dimensions of the raster on the specimen and the raster on the display device. Keeping display screen at a fixed size, higher magnification results from reducing the size of the raster on the specimen and vice-versa. The magnification is controlled by the current supplied to the x, y scanning coils or to the voltage supplied to the x, y deflector plates. Image magnification in an scanning electron microscope does not depend upon the power of the objective lens.

Resolution

The spatial resolution of the SEM depends on the size of the electron spot, which in turn depends on both the wavelength of the electrons and the electron optical system that produces the scanning beam. The resolution is also limited by the volume of the specimen material that interacts with the electron beam (*i.e.*, interaction volume). The spot size and the interaction volume are both large compared to the distances between atoms, so **the resolution of the SEM is not high enough to image individual atoms.**

Applications

In addition to topographical, morphological and compositional information, a SEM can detect and analyse surface fractures, provide information in micro structures, examine surface contaminations, reveal spatial variations in chemical compositions, provide qualitative chemical analysis and identify crystalline structures. SEM can be used for the study of parasites. SEMs can also be used as research tool in life sciences, biology, medical and forensic science, metallurgy, physical sciences etc. Scanning electron microscopes can be used for the production of semiconductor and microchips for computer industry. The SEM can observe bulk samples several centimeters in size and is consequently more flexible in its applications than the TEM.

Advantages

1. Wide array of applications.
2. Detailed 3D and topographical imaging.Can image comparatively bulky objects.
3. Fast and easy operation.
4. Versatile information obtained from different detectors.
5. Sample preparation is easy compared to TEM.
6. Data can be generated in digital form.
7. Interpretation of images is easy.

Drawbacks

1. SEMs are expensive, large and must be kept in an area free of any possible electric, magnetic or vibration interference.
2. Maintenance cost is high.
3. Special training is required to operate SEM.
4. There is risk of radiation exposure in it due to scattered electrons.
5. SEMs are limited to solid, inorganic samples small enough to fit inside the vacuum chamber that can handle moderate vacuum pressure.
6. Resolution limited to few *nm*.
7. Details on the atomic level can not be observed.

9.7. SCANNING PROBE MICROSCOPY (SPM)

It is a branch of microscopy which forms images of surfaces using a physical probe that scans the specimen. The first scanning probe microscope *i.e.*, the scanning tunneling microscope (STM) was developed by **Gerd Binnig** and **Heinrich Rohrer** is 1981. It is based upon the tunneling current between the conductive tip and the substrate (or sample). Another scanning probe microscope is

based upon the atomic force applied on the tip by the atoms of the sample and hence known as atomic force microscope (AFM). To form images, scanning probe microscope raster scan the tip over the surface. Many scanning probe microscopes can image several interactions simultaneously. The manner of using these interactions to obtain an image is called a mode. Their are two main modes of operation of scanning probe microscopes :

1. Constant interaction mode : In this mode of operation of an SPM, a feedback loop is used to physically move the probe closer to or farther from the surface under study to maintain a constant interaction. For scanning tunneling microscope, the interaction is the tunneling current whereas in case of contact mode AFM or in magnetic force microscope MFM, it is the cantilever deflection. The z -position of the tip (when scanning plane is xy) is recorded periodically and displayed as a heat map to give the topographical image of the sample.

2. Constant height mode : In this mode of operation of an SPM, the probe is not moved in the z-direction during the raster scan. Instead, the value of the interaction under study is recorded (*i.e.*, the tunneling current in case of STM or the cantilever oscillation amplitude for non contact AFM). This recorded information is displayed as a heat map and is called a constant height image. *Constant height imaging is much more difficult than constant interaction imaging because in this case probe is likely to crash into the sample surface.*

The probe in SPM, must have a very sharp apex. The sharper the probe, the better the resolution.

Advantages

1. The resolution is not limited by diffraction instead by the size of the probe-sample interaction volume. Hence, it has a great ability in measuring small local differences in object height.

2. The specimen do not require a partial vacuum but can be observed in air at standard temperature and pressure.

Drawbacks

1. The scanning techniques are slow due to slow scanning process.
2. The maximum image size is generally smaller.

Applications

1. In academic and industrial physics, chemistry and biology laboratories.
2. As standard analysis tools and as high level research instruments.

9.8. SCANNING TUNNELING MICROSCOPE

The scanning tunneling microscope (STM) is a type of scanning probe microscope and was developed by Gerd Binnig and Heinrich Rohrer in 1981. For this invention, they were awarded Nobel prize in Physics in 1986. An STM can produce

images with lateral resolution of 0.1 *nm* and depth resolution of 0.01 nm. **Thus it is capable of imaging and manipulating individual atoms within materials.** The STM can work in ultra high vacuum as well as in air, water, and various other liquid or gas ambients at a very wide range of temperatures (0°K to about 1250°K). The scan range for a STM is typically upto 1 μm with a scan speed of the order of few mm/min.

Principle

The STM is based on the concept of **quantum mechanical tunneling**. The scanning process is carried out by a probe that monitor electrons which tunnel between the surface of the specimen and the probe tip. The basic principle of the STM is sketched in Fig. 9.9. The scanning tunneling microscope utilizes a wire

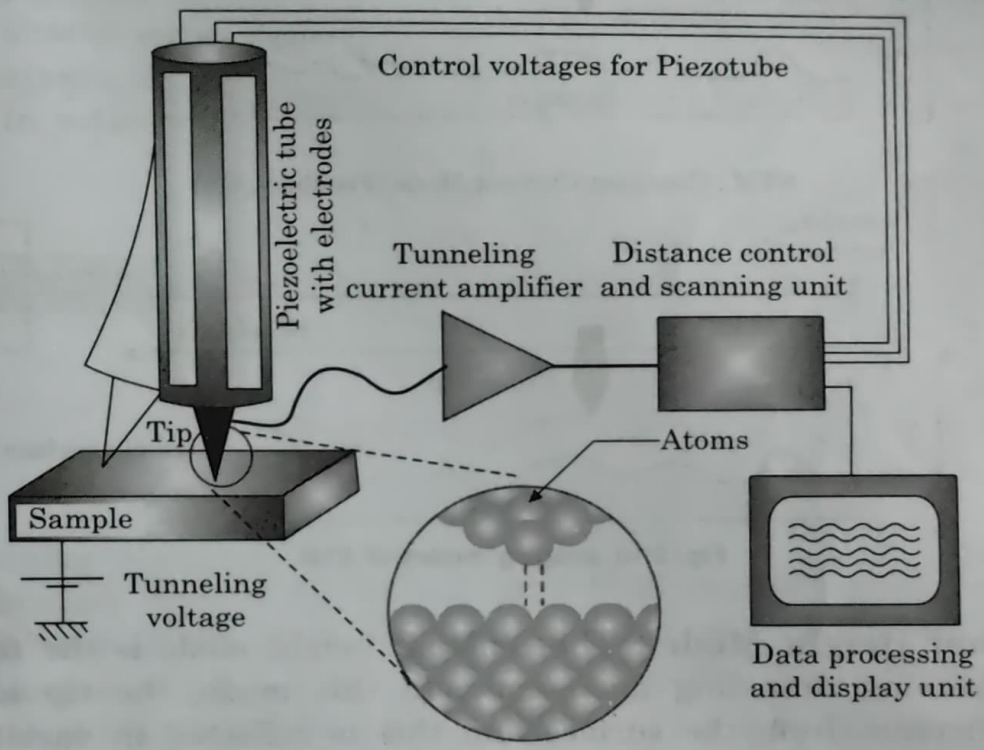


Fig. 9.9. Principle of STM

with a very fine point (tip). Since multiwall carbon nanotubes (MWNTs) are electrically conducting, they may be used as probes for an STM. This tip is positively charged and acts as a probe. When the separation between the tip and sample surface is about 1*nm*, electrons at individual surface atoms are attracted to the positive charge of the probe wire and tunnel (jump) into it. In this process, a small tunneling current typically in the sub-*nA* regime results. The probe wire is scanned back and forth across the surface in a raster pattern either in a **constant height mode** or **constant current mode**.

The **STM can only scan conducting surfaces** because it rely upon small tunneling current between tip and the sample. It is therefore, not used for non-conducting specimens.

I. Constant Current Mode : In the constant current mode, a feedback loop maintains a constant probe height above the sample surface profile, and the up/down probe variations are recorded. It is the **most widely used STM mode** but is **slower than the constant height mode.** This mode of operation assumes a constant (potential) barrier across the surface through which electron tunneling takes place. There is no risk of destroying the tip during the scan (fig. 9.10 b).

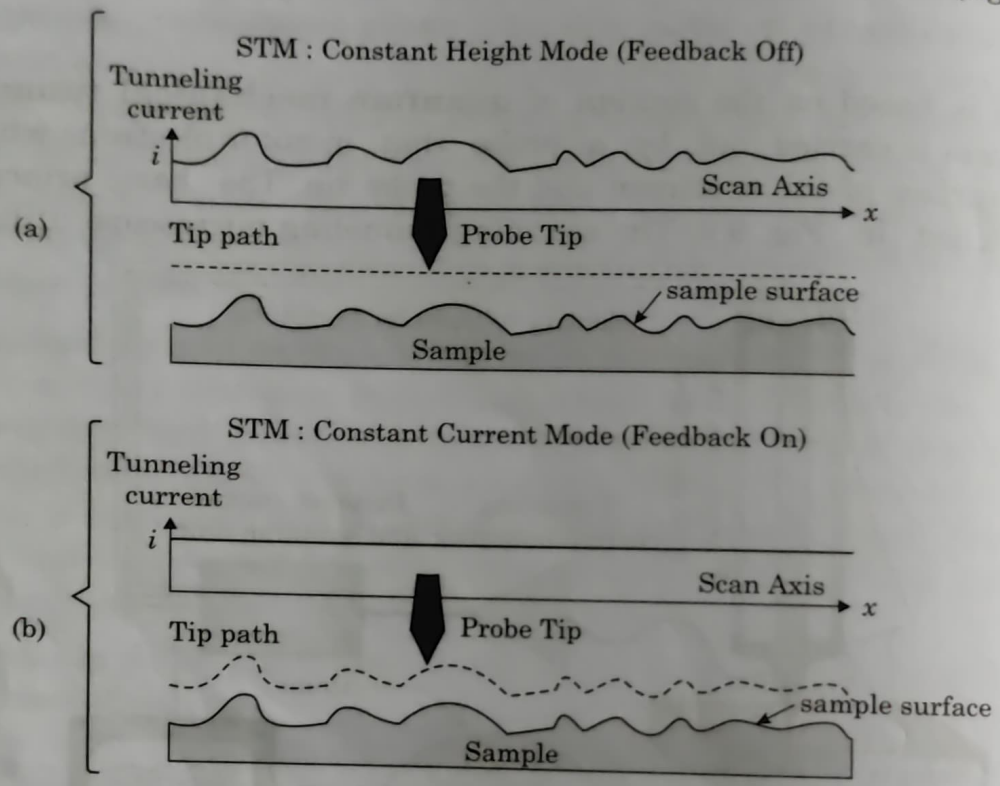


Fig. 9.10. Imaging modes of STM

II. Constant Height Mode : The constant height mode is the **fastest** scan **mode** of a scanning tunneling microscope. In this mode, the tip is constantly changing its distance from the surface and this is reflected in variations of the recorded tunneling current as the probe scans (fig. 9.10a). The feedback loop maintains the initial probe height, and is then turned off during the scan. The scanning probe provides a mapping of the distribution of the atoms on the surface. *The drawback of this mode is that, there is a risk that the tip will bump into unexpected high regions on the surface and be destroyed.*

The **resolution of an STM is high** because of the exponential dependence of the probe-surface atom separation d in the transmission coefficient, $T(\in) \approx \exp[-4\,kd]$ and hence in the tunneling current. *The tunneling current is very sensitive to the change in the separation d.* This makes the scanning tunneling microscope a very sensitive instrument. The tunneling current depends so strongly on the distance that it is dominated by the contribution flowing between the last atom of the tip and the nearest atom in the specimen.

A piezoelectric is a material in which an applied voltage in one direction makes the element longer or shorter in another direction. The scanning tunneling microscope utilizes a piezoelectric tripod scanner for the fine control of the tip in all the three dimensions when it is near to the sample. This piezoelectric tripod maintains the tip-sample separation d typically in the 0.4–0.7 nm range which is the equilibrium position between attractive ($0.3 < d < 1.0$ nm) and repulsive ($d < 0.3$nm) interactions. In this situation, the voltage bias causes the electrons to tunnel between the tip and sample.

The modern scanning probe microscopes use a tube geometry as shown in Fig. 9.11. Each of the four indicated sections can be made longer or shorter individually. If all four sections are made longer or shorter by the same amount, the tip moves in the z-direction. If the $+X$ side is made longer, and at the same time $-X$ side is made shorter by the same amount, the tube tilts, a little bit to one side. For small deformations, this makes the tip move primarily in the x- direction. The same can be done in y-direction also.

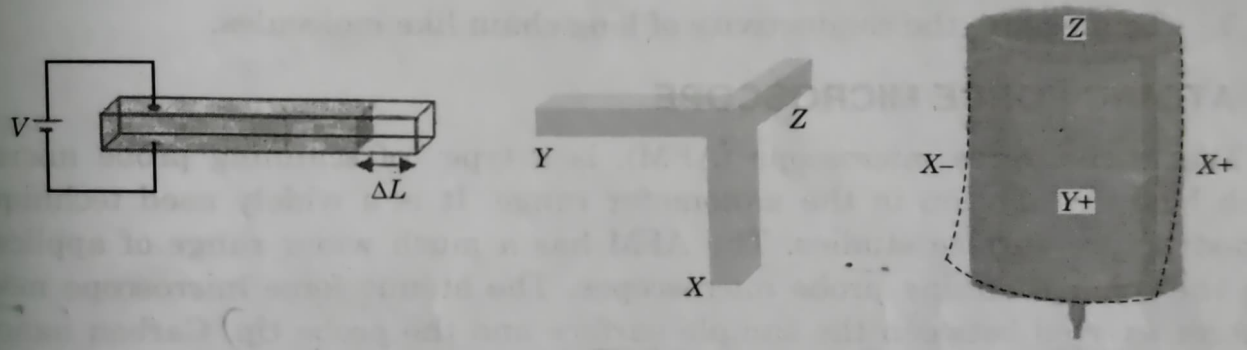


Fig. 9.11. Principle of piezo element in STM

The scanning tunneling microscope can also provide the information on the electronic structure at a given location in the sample by sweeping voltage and measuring current at a specific location. This gives a plot of the local density of states as a function of energy within the sample. The advantage of STM over other measurements of the density of states lies in its ability to make extremely local measurements.

Advantages

1. Its resolution (≈0.1nm) is better than AFM.
2. The tunneling current is very sensitive to the changes in the tip-sample separation (d). Hence STM is a very sensitive instrument.
3. Local density of electronic states can be measured very accurately.
4. STM has an atomically precise positioning system which allows very accurate atomic scale manipulation.

Drawbacks

1. It requires extremely clean and stable surfaces, sharp tips, excellent vibration control and sophisticated electronics which is quite challenging and therefore difficult to maintain.

2. The scanning tunneling microscope requires conductive samples or relatively conductive samples on a conductive substrate. It is not used with non-conductive samples.
3. Scanning is a slow process of imaging.

Applications

1. The STM can be used to investigate the discrete atomic like states of colloidal quantum dots and other systems.
2. To investigate coulomb blockade and coulomb staircase phenomena.
3. To image and manipulate individual atoms in a sample.
4. As a spectrometer for measuring electronic energies.
5. Can provide information on the topography and defect structure of a surface over distances close to the atomic scale.
6. In atomic deposition of metals (gold, silver, tungsten etc.) with any desired pattern.
7. To measure the conductivity of long chain like molecules.

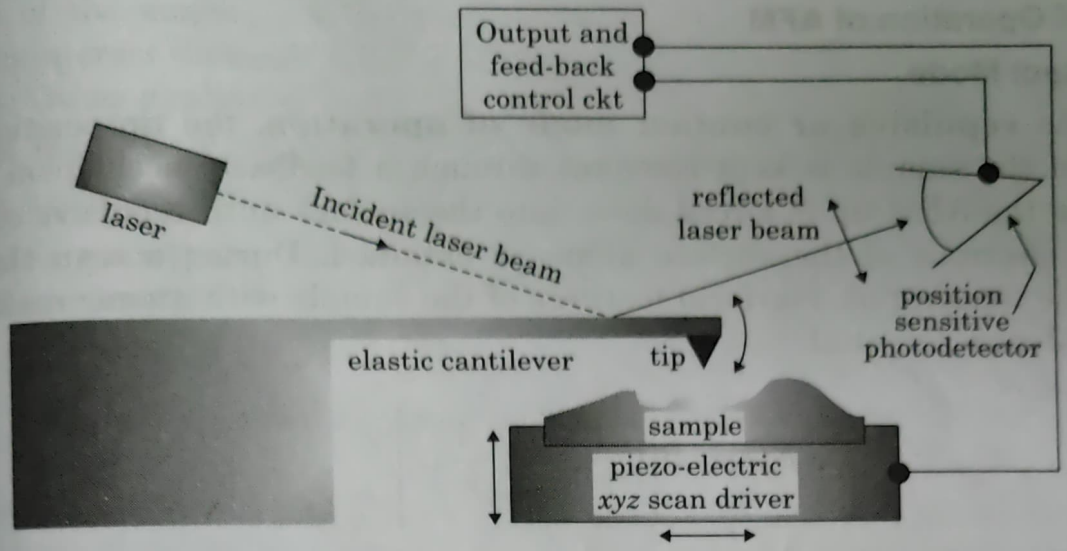
9.9. ATOMIC FORCE MICROSCOPE

The atomic force microscope (AFM), is a type of scanning probe microscope which has a resolution in the nanometer range. It is a widely used technique for nano-structure surface studies. The AFM has a much wider range of applicability than the other scanning probe microscopes. The atomic force microscope monitors the force exerted between the sample surface and the probe tip. Carbon nanotubes are used as tip material. AFM can be used to observe and manipulate nanometer sized objects of **conductive and insulating nature.** It can work in vacuum, air, gaseous and liquid environments.

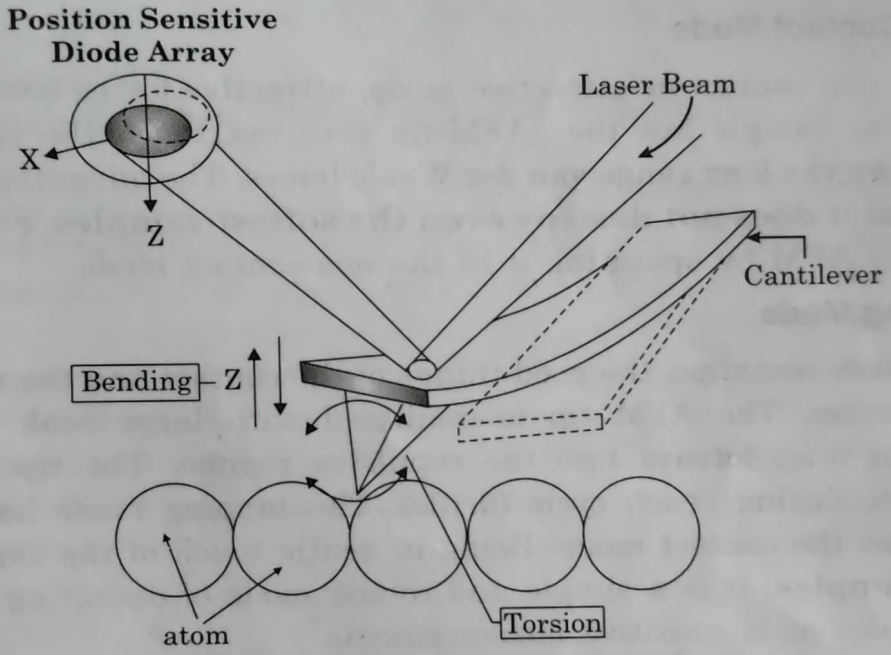
Principle

A sketch of an AFM experiment is shown in Fig. 9.12 a. It consists of a nanometer sized tip mounted on a **sharp silicon** or SiO_2 or **silicon nitride** elastic cantilever. Cantilevers are fabricated by photolithographic methods. They are typically 100 μm long and 1 μm tick. A piezoelectric *xyz* scan driver is used to scan the tip across the sample. This tip is brought close to the surface of the sample under study so that atomic forces occur between tip and the sample. The distance between the tip and the sample can be anywhere between 0 and 100 nm. These atomic forces can be either repulsive or attractive. The force acting on the tip is function of the topography and contents of the surface of the sample and changes during the scan which causes in a position dependent deflection of the elastic cantilever.

The deflection produced in the cantilever is monitored by reflecting a laser beam on the cantilever and recording the movement of the reflected beam with a position



(a) Sketch of AFM



(b) Enlarged view of cantilever and tip

Fig. 9.12

sensitive photodetector. The atomic force microscope is sensitive to the vertical component of the surface forces. The signal from the photodetector can be used in a feedback loop with the *xyz* scan driver and the motion of the tip can be controlled.

The spring constant (usually between 0.1 and 1.0 N/m) of the cantilever should be small enough so that minute atomic forces can be detected. The **tip should be as sharp as possible** to provide atomic resolution. To minimize sensitivity of AFM to external mechanical vibrations, **the resonance frequency of the cantilever should be as high as possible.** The tip should be as narrow as possible so that it can penetrate into deep troughs on the surface of the sample. Small cantilevers fulfill the requirements of small spring constant and high resonance frequency. Silicon is used for fabricating such cantilevers.

Modes of Operation of AFM

1. Contact Mode

In the **repulsive or contact mode of operation**, the tip position over the surface of the sample is kept constant through a feedback mechanism (9.13b). In this mode the AFM tip is forced down into the surface until repulsive contact with the core electrons of the surface atoms is obtained. During a scan the AFM tip follows the topographic (surface) features of the sample with atomic resolution. The Lennard-Jones potential

$$E(r) = B\left[\left(\frac{A}{r}\right)^{12} - \left(\frac{A}{r}\right)^{6}\right]$$

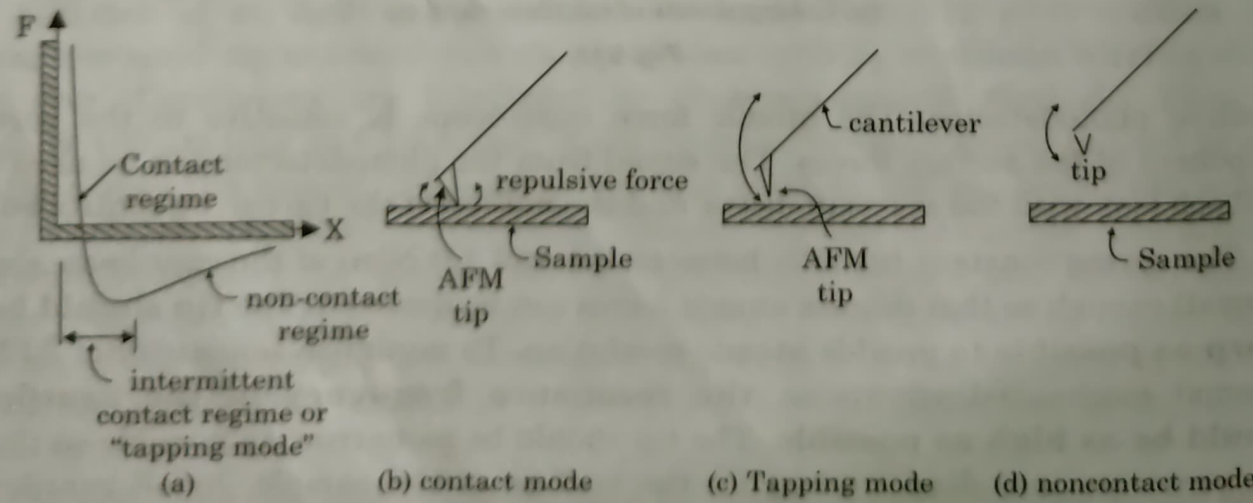
is supposed to give rise to this core-to-core repulsive force.

2. Non-Contact Mode

In the non contact or attractive mode, attractive forces bend the tip bringing it closer to the sample but the AFM-tip does not touch the surface (9.13d). It is influenced by the long range van der Waals forces. The advantage of the non-contact mode is that it **does not destroy even the softest samples**. So, soft specimens are analysed by AFM by operating it in the non-contact mode.

3. Tapping Mode

This mode combines the good things of the contact and the non-contact mode of AFM operation. The AFM tip is oscillated with large peak to peak amplitude resulting in brief forrays into the repulsive regime. The tip gently touches the sample once during each cycle (9.13c). The tapping mode has nearly the same resolution as the contact mode. Being in gentle touch of the sample, **can be used for soft samples**. It is a simple and robust mode of operating the AFM. Tapping mode provides most sensitive measurements.



(a) (b) contact mode (c) Tapping mode (d) noncontact mode

Fig. 9.13.

In any of the modes, the attractive or repulsive forces plus response of the system to counteract them are used as a means of generating a topographic image of the sample. Other applications of AFM are :

- AFM can be used to move individual nano-structures.
- As a tool to scratch surfaces and make nano-scale patterns.

The other variations of this probe technique are magnetic force microscopy (MFM) and electrostatic force microscopy (EFM) in which the force applied on the tip by the atoms of the sample is magnetic or electrostatic respectively.

REVIEW QUESTIONS

1. Discuss the limitations of optical microscopes for the observation of very small objects.
2. Define limit of resolution of a microscope. Show that limit of resolution of electron microscope is much smaller than that of optical microscope.
3. Explain Rayleigh's criterion of resolution. Why electrons are suitable to be used as illumination in microscopes ?
4. Define optical microcopy. What are the various factors that affect the resolving power of an optical instrument ?
5. Discuss the working principle of a transmission electron microscope (TEM). What type of information it can provide about the sample ?
6. Discuss about the possible applications of TEM. Also mention its advantages and disadvantages.
7. What is a scanning electron microscope (SEM) ? What are the various signals produced by scanning electron microscope ?
8. Give the schematic diagram of a SEM and discuss its working. What is its most common or standard detection mode ?
9. What are back scattered electrons in a SEM ? How they are useful in SEM imaging ? What information they provide about the topography of a sample ?
10. Define magnification of a SEM. How the magnification can be improved in a SEM ?
11. cuss about the possible applications of a scanning electron microscope (SEM). What are advantages and drawbacks of a SEM ?
12. at do you understand by scanning probe microscopy (SPM) ? How images are formed in a anning probe microscope ? What are the two modes of operation of SPMs ?
13. Discuss the principle of a scanning tunneling microscope (STM). How a STM works in constant height mode ? Why the resolution produced in STM is high ?
14. Discuss the applications of a scanning tunneling microscope (STM). What are its advantages and drawbacks ?
15. What is a atomic force microscope (AFM) ? Give its principle and state the conditions imposed on spring constant and resonance frequency of the cantilever for better performance of AFM.

What are the various modes of operation of an AFM ? Why a low value of spring constant of cantilever is desirable ?

oftenly found than hcp. Studies regarding crystal structure are important because certain properties of nanostructures depend on their crystal structure.

Table 8.1 : Crystal systems and Associated Space Groups in 2D

S. No.	System	Parameters	No. of Space Groups (Symmetry elements)
1.	Oblique	$a \neq b, \gamma = 90°$ or $(a = b, \gamma \neq 90°, 120°)$	2
2.	Rectangular	$a \neq b, \gamma = 90°$	7
3.	Square	$a = b, \gamma = 90°$	3
4.	Hexagonal	$a = b, \gamma = 120°$	5

Table 8.2 : Crystal systems and Associated Space Groups in 3D

S. No.	System	Parameters	No. of Space Groups (Symmetry elements)
1.	Triclinic	$a \neq b \neq c; \alpha \neq \beta \neq \gamma$	2
2.	Monoclinic	$a \neq b \neq c; \alpha = \gamma = 90° \neq \beta$	13
3.	Orthorhombic	$a \neq b \neq c; \alpha = \beta = \gamma = 90°$	59
4.	Tetragonal	$a = b \neq c; \alpha = \beta = \gamma = 90°$	68
5.	Trigonal	$a = b = c; \alpha = \beta = \gamma < 120° \neq 90°$	25
6.	Hexagonal	$a = b \neq c; \alpha = \beta = 90°, \gamma = 120°$	21
7.	Cubic	$a = b = c; \alpha = \beta = \gamma = 90°$	36

8.3. X-RAY CRYSTALLOGRAPHY

The atomic and molecular structure of a crystal can be determined by the technique of X-ray crystallography. A collimated beam of X-rays is directed at the crystal and the atoms of the crystal cause diffraction of X-rays into many specific directions (Fig. 8.1). By measuring the angles and intensities of these diffracted beams, a three dimensional (3D) picture of the density of electrons within the crystal can be formed. **This provides information regarding the mean positions of the atoms in the crystal, their chemical bonds, their disorder etc.** X-rays are diffracted by various planes of atoms in crystal because their wavelength λ is of the order of inter planar separation d in the crystal. The wavelength of X-rays is given by

$$\lambda = \frac{1.240}{E} \text{nm} \quad \ldots(1)$$

where E is the energy of X-rays in KeV.

The specular or coherent or Bragg reflection of X-rays from successive planes of the crystal is governed by the Bragg's law which is

$$2d \sin\theta = n\lambda \quad \ldots(2)$$

where θ is the angle that the X-ray beam makes with the plane of atoms and n is an integer, $n = 1, 2, 3, \ldots\ldots$.

Usually the beam is kept fixed in direction and the crystal is rotated through a broad range of angles to record the X-ray diffraction scan.

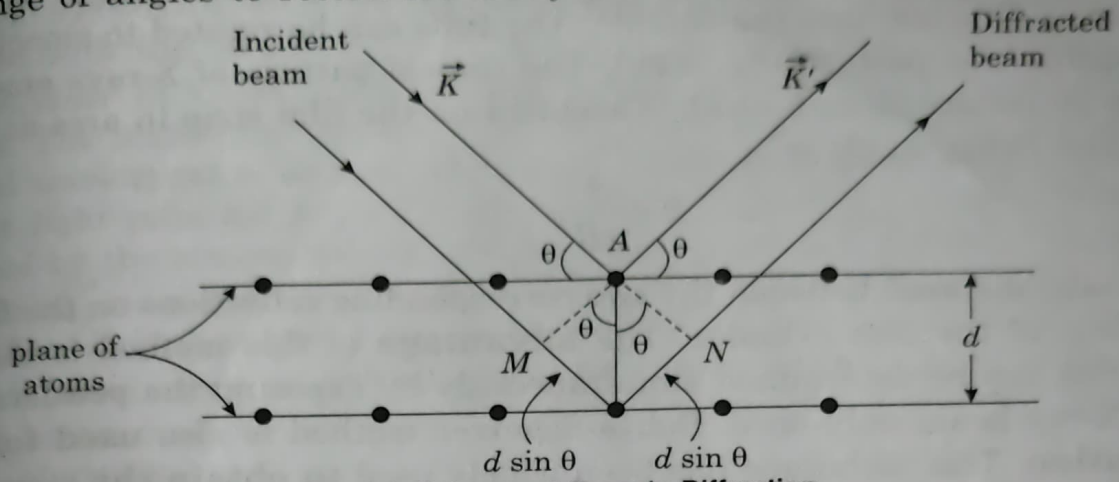


Fig. 8.1. Scheme of Bragg's Diffraction

The crystal planes are denoted by indices h, k, l called the **Miller indices.** The inter-planar separation d in simple cubic crystals, is given by

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \qquad \ldots(3)$$

where a is the **lattice constant** of cubic crystal. The planes with higher h, k, l values are closer together and hence have larger Bragg diffraction angles θ. *The relative amplitudes of X-ray lines from different crystallographic planes help in identifying the type of structure.* For a bcc lattice, diffraction peaks are observed only for planes for which $(h+k+l)$ is an even integer whereas for fcc lattice, diffraction peaks are observed when either h, k, l are all odd integers or all even integers.

X-ray spectra are recorded for rotations of the crystal around the mutually perpendicular planes of the crystal to provide comprehensive information on various crystallographic planes.

Fourier transforms are used to find the positions of atoms in the unit cell. This procedure identifies the space group associated with the structure and provides the length of lattice constants a, b, c of the unit cell and also the values of angles α, β, γ between them.

The **widths of the Bragg peaks** of the X-ray scan of a sample provides information on the **average grain size** of the sample, however a transmission electron microscope (TEM) is needed for the actual determination of grain size.

X-ray crystallography is **a form of elastic scattering** because the outgoing X-rays have the same energy and wavelength as the incoming X-rays. It is a chief method for characterizing the atomic structure of new materials.

Advantages

- SAXS is an accurate method for structure determination of materials
- It is a non-destructive technique and hence no damage to the samples occur
- It can provide quantitative measurement
- Samples can be small
- The measurement process can be fast according to the X-ray source used
- Minimum sample preparation is needed
- In-situ measurements can be done.

Disadvantages

- Expensive instrumentation
- Low information content in SAXS data
- Complex data analysis.

Applications

- SAXS can be used as a diagnostic tool in two ways i.e. either as angular dispersive in which monoenergetic X-rays are used and scattering at various angles is recorded or as energy dispersive in which polyenergic X-rays are used and scattering at certain angle ? is recorded
- SAXS is a reliable method to differentiate between normal and cancerous tissues
- For structure determination of soft matter such as polymers or colloids
- For studying nano composites, metals, minerals etc
- To study about biological macromolecules e.g. proteins or other bio macromolecules in solution, macromolecule conformation, protein aggregation etc
- To study lattices of nano objects such as nanoscale superlattices.

Solved Examples

Ex. 1. ***Find the glancing angle on the (110) plane of a cube of rock salt corresponding to second order diffraction maximum for the X-rays of wavelength 0.071 nm. The lattice constant for rock salt is 0.281 nm.***

Sol. In cubic crystals, the interplanar spacing

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

where a is the lattice constant of the crystal and h, k, l are the Miller indices of the set of planes under consideration. In this case,

$$(h, k, l) = (1, 1, 0)$$

$$a = 0.281 \text{ nm}$$

$$\lambda = 0.071 \text{ nm} \qquad \text{and} \quad n = 2$$

$$\therefore \quad d = \frac{a}{\sqrt{1^2 + 1^2 + 0^2}} = \frac{a}{\sqrt{2}} = \frac{0.281}{\sqrt{2}} \text{ nm}$$

From Bragg's law

$$2d \sin\theta = n\lambda$$

$$\therefore \quad \sin\theta = \frac{n\lambda}{2d}$$

For glancing angle, θ is very small, therefore

$$\theta \approx \sin\theta = \frac{n\lambda}{2d}$$

Substituting various values, we get

$$\theta \simeq \frac{2 \times 0.071}{2 \times \left(\frac{0.281}{\sqrt{2}}\right)} = \frac{0.071 \times \sqrt{2}}{0.281}$$

$$= \frac{0.071 \times 1.414}{0.281} = 0.35727 \text{ radian}$$

or $$\theta = 0.35727 \times \frac{180^\circ}{\pi} = \frac{0.35727 \times 180^\circ}{3.14}$$

$$\theta \simeq 20.5^\circ$$

Ex. 2. ***The first few lines in the powder pattern of a cubic crystal have the following S-values : 49.2, 56.4, 80.8, 96.0, 100.4 mm. The radius of the film cylinder (R) is 57.3 mm, and the wavelength of the X-ray beam used is 1.542 Å. Determine the structure and lattice constant of the crystal.***

Sol. Given that

S-values : 49.2, 56.4, 80.8, 96.0, 100.4 mm

Radius R of the film cylinder = 57.3 mm

Wavelength of X-rays, λ = 1.542 Å

In cubic crystals, interplanar separation

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \qquad \ldots (1)$$

where a is the lattice constant of the crystal and (h, k, l) are the miller indices of reflecting planes.

Further

$$2d \sin\theta = n\lambda$$

$$\sin\theta = \frac{\lambda}{2d}, \quad n = 1$$

or $$\sin^2\theta = \frac{\lambda^2}{4d^2} = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2) \qquad \ldots (2)$$

on using equation (1).

Since λ is fixed, therefore

$$\sin^2\theta \propto (h^2 + k^2 + l^2)$$

Also $$\sin\theta \approx \theta = \frac{S}{4R}$$

Substituting various S-values and the fixed value of R, we get

$$\sin^2\theta_1 = \left(\frac{S_1}{4R}\right)^2 = \left(\frac{49.2}{4\times 57.3}\right)^2 = 0.04608$$

$$\sin^2\theta_2 = \left(\frac{S_2}{4R}\right)^2 = \left(\frac{56.4}{4\times 57.3}\right)^2 = 0.06055$$

$$\sin^2\theta_3 = \left(\frac{S_3}{4R}\right)^2 = \left(\frac{80.8}{4\times 57.3}\right)^2 = 0.12428$$

$$\sin^2\theta_4 = \left(\frac{S_4}{4R}\right)^2 = \left(\frac{96.0}{4\times 57.3}\right)^2 = 0.17543$$

$$\sin^2\theta_5 = \left(\frac{S_5}{4R}\right)^2 = \left(\frac{100.4}{4\times 57.3}\right)^2 = 0.19188$$

These $\sin^2\theta$ values are in the ratio of integral numbers as

$$3 : 4 : 8 : 11 : 12$$

i.e. $$(1^2+1^2+1^2) : (2^2+0^2+0^2) : (2^2+2^2+0^2) : (3^2+1^2+1^2) : (2^2+2^2+2^2)$$

Since these values are proportional to $(h^2 + k^2 + l^2)$ values, therefore the possible (h, k, l) values are

(111); (200); (220; (311) and (222)

These planes are possible in fcc crystal structure. Hence the cubic crystal under consideration is fcc.

The lattice constant of the crystal may be calculated from

$$a^2 = \frac{\lambda^2}{4\sin^2\theta}(h^2 + k^2 + l^2)$$

$$= \frac{(1.542)^2}{4\times 0.04608}(1^2 + 1^2 + 1^2)$$

$$a^2 = 38.7005$$

$$\therefore \quad a = 6.3 \text{ Å}$$

Ex. 3. The Bragg angle corresponding to the first order reflection from (111) plane in a crystal is 30° when X-rays of wavelength 1.75 Å are used. Calculate the lattice constant (i.e. interatomic spacing) of the crystal.

Sol. The interplanar spacing is given by

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

For (111) planes

$$d_{111} = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{a}{\sqrt{3}}$$

But from Bragg's law

$$2d \sin\theta = n\lambda$$

or $$2 \times \frac{a}{\sqrt{3}} \sin 30° = 1 \times 1.75 \times 10^{-10}$$

or $$2 \times \frac{a}{1.732} \times \frac{1}{2} = 1.75 \times 10^{-10}$$

or $$a = 1.732 \times 1.75 \times 10^{-10} \text{ m}$$

or $$a = 3.031 \times 10^{-10} \text{ m} = 3.031 \text{ Å}$$

REVIEW QUESTIONS

1. Explain Bragg's diffraction law and discuss the importance of X-rays in getting information about crystals.
2. What is X-ray crystallography? Discuss its importance in the determination of crystal structure.
3. Describe an X-ray diffraction method suitable for samples in powder form. Which method is used for sample identification ?
4. Discuss about the Debye-Scherrer method of X-ray diffraction. What information can be obtained by this method about the crystals ?
5. What are the various methods for determining particle sizes in different structures ? Describe about one such method based on mass spectrometry.
6. Discuss about the low energy electron diffraction (LEED) technique of obtaining surface information of single crystals.
7. What is reflection high energy electron diffraction (RHEED) ? What is its use ?
8. What are the various causes that increase the width of XRD peaks of nanoparticles ?
9. Differentiate between instrumental broadening and broadening due to sample imperfection for XRD peaks.
10. Explain "blue shift" in absorption spectra peaks of nanoparticles.
11. Discuss about the shift in photoluminescence (PL) peaks of nanoparticles.
12. Describe about small angle *X*-ray diffraction method of molecular structure determination. What are its limitations ?
13. Briefly describe about the SAXS. What are its advantages over crystallography ? State its various applications.

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